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BY S. LAWRENCE BIGELOW AND E. ROGER WASHBURN**

Of all methods for measuring surface tension, the rise of liquids in capillary tubes is the simplest in application and in theory. But frequently it appears to be impossible to reproduce results with reasonable accuracy, while the cause of the trouble is not apparent. On this account the method seems to be falling into disfavor; which is unfortunate.

We undertook to discover, if possible, what some of these hidden difficulties might be and how to guard against them. We were successful in bringing to light some sources of error and in showing that they can be avoided by the application of simple precautions.

In this article we deal mainly with variations in the surface tensions of solutions with time.

Historical

A number of instances of such variations have been recorded in the literature. As early as 1869, A. Dupré,¹ while studying the surface tensions of aqueous solutions of soap, as shown by the vertical height to which fine jets of the solution rose under a definite pressure, conceived the idea that the surface tension of a freshly formed surface was greater than that of older surfaces.

Some twenty years later, Lord Rayleigh,² without previous knowledge of Dupré's work, reached the same conclusion. He measured the surface tensions of solutions of sodium oleate and of saponin, using the vibrating jet method for the freshly formed surfaces and the capillary rise method for the older surfaces. He showed that only in the older surfaces did the soap or saponin produce marked lowering. He believed this lowering to be due to the formation of an insoluble layer or "pellicle" of the organic material on the surface.

S. R. Milner,³ studied the phenomenon with sodium oleate solutions in greater detail. He observed that the fall in surface tension was most rapid at first, and then became slower until finally a constant value was reached. The more concentrated the solution the quicker it reached this constant value. Agitation reestablished the initial value and then the phenomenon repeated itself, but did not always result in the same minimum. He concluded that the decrease in surface tension is caused by adsorption of sodium oleate in the surface until a definite concentration is reached. This would occur quickly with concentrated solutions but might require hours when they were dilute.

* Contribution from the Chemical Laboratory of the University of Michigan.

** The work presented in this paper is taken from a dissertation presented by E. Roger Washburn in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the University of Michigan.

¹ A. Dupré: *Théorie mécanique de la Chaleur* (1869).

² *Proc. Roy. Soc.*, **47**, 281 (1890).

³ *Phil. Mag.*, (6) **13**, 96 (1907).

L. Berzeller,¹ observed a similar decrease in the surface tension of soap solutions with time.

P. Lecomte du Noüy² is the author of several papers and a book describing instances of surface tensions falling with time. He developed an instrument utilizing the method wherein the force is measured which is required to pull a wire ring off the surface of a liquid. He found, for example, that dog serum added to water or to a saline solution reduced the surface tension gradually. The maximum lowering was reached in from twenty to thirty minutes. Agitation produced an increase in the surface tension but not up to the original value. A second fall ensued but not to so low a value. Repetition gave variations between narrower and narrower limits until finally the surface activity of the serum (its ability to lower surface tension with time) seemed to be completely lost. This lessening of range of variations, this damping effect, must be due to some chemical reaction. Du Noüy says that all of the effects he observed may be due to one or more of the following causes; chemical change, adsorption in the surface, adsorption by colloids in the liquid, modification of molecular arrangement in the surface.

His results are most interesting, but the systems with which he works are complex and contain too many variables. We need careful studies with the simplest possible systems to establish fundamental principles before we can interpret such results as his with confidence.

He makes the following remarkable statement; "It is only through the ring method that it is possible to observe and study this phenomenon (changing surface tension) as it is the only procedure which permits the measurement of the surface tension of the same layer of liquid at very short intervals." This is manifestly in error. As has been said, S. R. Milner studied the change in surface tension by the capillary rise method which is obviously superior because the surface is not disturbed. Pulling off a ring and replacing it must seriously upset any molecular arrangement in the surface or any concentration gradient established by adsorption. It is indeed surprising that du Noüy succeeded in obtaining the results he did.

C. E. Davis, H. M. Salisbury and M. T. Harvey,³ using the drop weight method, observed a slight decrease in the surface tension of gelatin solutions with time. Here again it is surprising that the effect was observed, for during the formation of drops the surface is constantly agitated, and we and others have always observed that agitation tends to restore the initial values.

A study of the change of surface tension of solutions of gelatin, casein, albumin and haemoglobin has been made by J. M. Johlin⁴ applying both the drop weight and the capillary rise methods. He found that the longer the time he allowed for each drop to form, the greater the observed change in surface tension. This is quite as it should be, and is convincing evidence that the method is unsuited for anything but qualitative purposes.

¹ Internat. Z. physik. Chem. Biol. 1, 124 (1914).

² J. Exp. Med., 35, 575, 707; 36, 113 (1922); Science, 59, 580, 1539; "Surface Equilibria of Biological and Organic Colloids" (1926).

³ J. Ind. Eng. Chem., 16, 161 (1924).

⁴ J. Phys. Chem., 29, 270, 897, 1129 (1925).

His results with the capillary rise method were somewhat irregular, especially when wide capillaries were used. Frequent "throbbing" of the meniscus he ascribed to molecular rearrangements in the surface. He observed that often a period of inactivity intervened before the fall began. This lasted but a few seconds with moderately concentrated solutions but grew longer as the dilution was increased. We shall refer to this again in the description of our own work.

It is obvious from this brief review that the phenomenon is of especial interest to physiologists, and with good reason, as it doubtless plays important roles in life processes. Substances such as gelatin, albumin, serum and the like are too indefinite and solutions containing more than one solute are too complex to serve for the establishment of the underlying principles on a satisfactorily convincing basis. A study of the phenomenon as shown by the simple solutions of well-defined chemical compounds is needed, and this we hope we have, in a measure, supplied.

Apparatus and Methods

We adopted as our model the apparatus and methods so ably developed and described by T. W. Richards¹ and his co-workers and endeavored to maintain their standards of accuracy in our work.

We employed the customary methods and had the customary difficulty in selecting a few short lengths of capillary tubing of satisfactorily uniform bore. The range, which careful calibration proved to be uniform in bore, was included between two rings etched in the glass. These tubes were fashioned into capillarimeters of the type shown in Figs. 1, 2, 3, and 4.

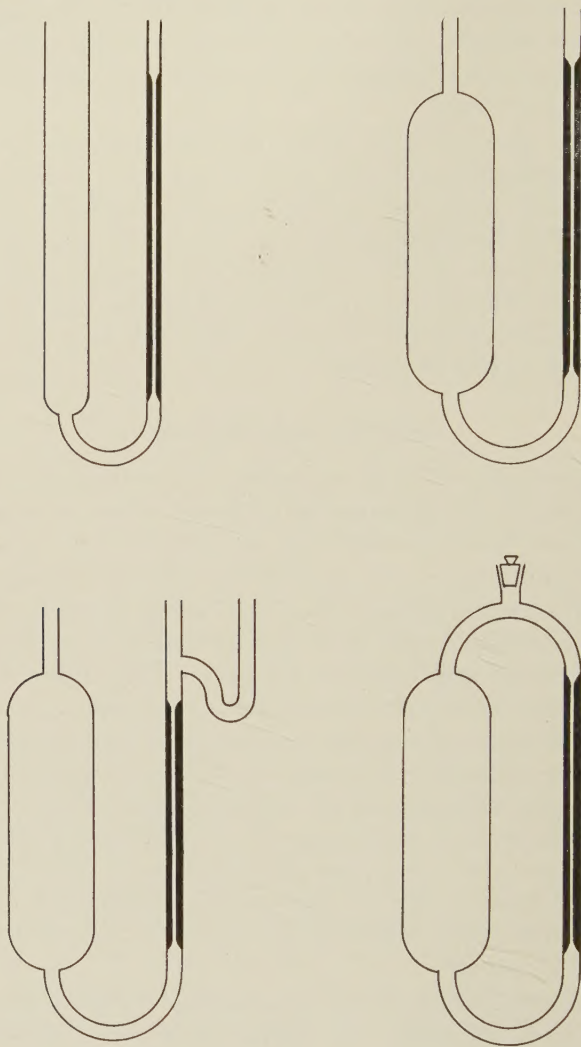
In type 1 the wider reference tube is not so wide that the capillary ascension in it can be neglected. The correction is easily applied in most cases, but with constantly changing surface tensions it introduces an inconvenient complication. Therefore we used these only for preliminary work. All of our final measurements were made with capillarimeters of types 2, 3, and 4, the reference tubes of which were at least 38 mm. in diameter. Richards has found that in a tube of this diameter, the central portion of a water meniscus is essentially a flat surface.

The capillarimeters were used in a thermostat which was fitted with plate glass windows front and back. An opaque shield placed between the capillarimeter and the electric light in the rear and just below the level of the large meniscus, as recommended by Richards, aided materially in giving sharply defined images. The cathetometer was graduated to read to 0.05 mm. Its telescope was equipped with a 72 mm. microscope objective, which gave a clear cut, magnified view of the meniscus.

Following the usual precaution, the meniscus was raised and lowered several times and then allowed to fall to its equilibrium position before a first reading was taken. This raising and lowering was produced by blowing or drawing

¹ J. Amer. Chem. Soc., 37, 1670 (1915); 43, 834 (1921).

through a train of calcium chloride, soda lime and cotton connected to the wide arm of the capillarimeter so there was no chance of contaminating the capillary meniscus.



FIGS. 1-4

We designated our capillaries by letters and determined their radii by the usual method of measuring the lengths and weights of threads of mercury, too well known to require description. We also determined their radii by observing the capillary rise of water and substituting in the equation $rh = a^2$, where r is the radius sought, h the true or corrected height to which water rises and a^2 is its capillary constant. Richards and Carver¹ obtained for this constant, at 20° the value 14.877 which we used.

¹ J. Am. Chem. Soc., 43, 834 (1921).

Our results by the two methods checked satisfactorily. For example, we found the radius of capillary C by the mercury thread method to be 0.0169 cm.; by the surface tension method we found 0.0166 as a minimum and 0.0167 cm. as a maximum. The radius of capillary 1P we found by the mercury thread method to be 0.0210 cm. (minimum) 0.0211 cm. (maximum); by the surface tension method we found 0.0211 cm. (minimum) and 0.0212 cm. (maximum). Agreement being so close we felt the surface tension method was sufficiently reliable and preferred it because of the accurate temperature control in the thermostat and because it is so much more easily and rapidly carried out.

The cleaning of the tubes is important. We tried the usual cleaning agents such as aqua regia and chromic acid but finally concluded that the most consistently good results could be obtained by the following procedure. Hot alkaline permanganate solution is drawn through the tube for several minutes, followed by hot hydrochloric acid to dissolve any manganese dioxide formed. Hot water is then drawn through the tube for fifteen or twenty minutes. The tube is dried in an electric oven, the last traces of moisture being removed by drawing dry, filtered, air through the hot tube.

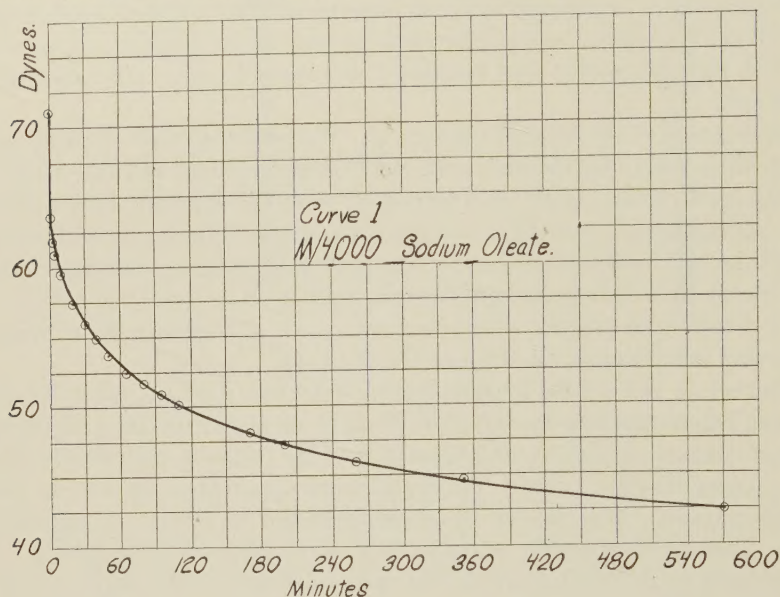
Whether or not a tube is clean can be determined by the behavior of the meniscus before starting an experiment. The meniscus is blown up, through the train already described, and then falls evenly with no indication of sticking, to its equilibrium point. The walls drain apparently dry and no visible droplets remain. It is drawn down and allowed to rise to its equilibrium point. This must coincide exactly with that obtained after falling. The motion must be perfectly smooth and there must not be the slightest flattening or other distortion of the meniscus when in motion. If these conditions are fulfilled the tube is adequately clean.

Making ready for an experiment we poured into the wide arm of the capillarmeter enough of the solution to cause the meniscus in the capillary to stand at some point between the etched lines which marked the uniform section of the tube, and then fastened it vertically in the water of the thermostat. By blowing and suction the meniscus was caused to rise and fall and its behavior studied critically. After enough time had elapsed for the temperature of the apparatus to reach that of the bath, the solution was vigorously agitated and the first reading was made of the meniscus in the capillary and immediately thereafter of the level in the reference arm. Other readings were taken as often as seemed necessary to follow the changes being observed. The meniscus was not agitated after the first reading was made unless so stated in the reports of the results.

In order to abbreviate our report and to facilitate comparisons of results obtained with different tubes, we have omitted the cathetometer readings and capillary heights, but have calculated the corresponding surface tensions in each case according to the formula, $\gamma = \frac{1}{2}ghr(D-d)$, wherein γ is the surface tension, g , the gravitational constant, h , the corrected rise, r , the radius of the tube, and $(D-d)$, the difference between the densities of the liquid and vapor phases. With dilute aqueous solutions this value is almost

exactly the difference between the density of water and that of air saturated with water vapor. And so we used this value; the error thus introduced is negligible as will be shown later.

Solutions of Sodium Oleate. All of our solutions were made up by weight. The sodium oleate was obtained from Mallinckrodt. It was not further purified by us, but was dried at 90° to constant weight. The greater part of

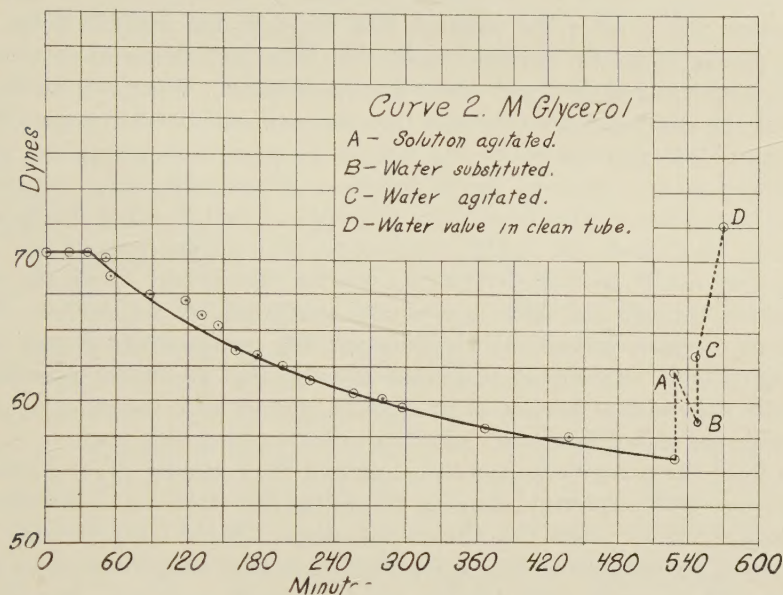


the work which we carried out with this substance was completed in 1924, before the publication of the experiments by J. M. Johlin (loc. cit.). The results which we obtained agree essentially with his, especially as to maximum and minimum values, and we experienced the same difficulty in reproducing exactly any particular experiment carried out with very dilute solutions. The rate of fall which we observed was somewhat slower than that observed by Johlin, though the difference is not great considering the difficulty of working with dilute solutions of this material in fine capillary tubes. Following are the details and results of one of these experiments selected as typical of the many which we did.

Time elapsed	Surface tension	Time elapsed	Surface tension
0	71.0 dynes	65 minutes	52.5 dynes
1 minute	63.7 "	80 "	51.7 "
3 minutes	61.9 "	95 "	50.8 "
5 "	61.0 "	110 "	50.2 "
10 "	59.6 "	170 "	48.2 "
20 "	57.5 "	200 "	47.3 "
30 "	56.0 "	260 "	46.0 "
40 "	54.9 "	350 "	44.7 "
50 "	53.7 "	570 "	42.4 "

These results are plotted as Curve 1.

Solutions of Glycerol. The glycerol was purified by repeated fractional distillation under reduced pressure; the fraction which we used distilled at 200° (uncorrected) under 35 mm. pressure. It is particularly difficult to reproduce an experiment with solutions of glycerol. The reasons for this we do not surely know but we shall offer a possible explanation of the apparently erratic behavior after presenting the experimental data.



Time elapsed	Surface tension	Time elapsed	Surface tension
0	70.7 dynes	179 minutes	63.5 dynes
19 minutes	70.7 "	199 "	62.7 "
34 "	70.7 "	221 "	61.7 "
49 "	70.3 "	231 "	61.2 "
54 "	69.0 "	258 "	60.8 "
87 "	67.8 "	283 "	60.4 "
119 "	67.4 "	298 "	59.8 "
130 "	66.3 "	368 "	58.3 "
143 "	65.5 "	438 "	57.7 "
159 "	63.8 "	528 "	56.0 "

These results are plotted as Curve 2.

After the last reading the solution in the capillarmeter was agitated by drawing it down and blowing it up in the capillary. This caused the surface tension to rise to 62.2 dynes, (point A on the curve). The solution was then carefully withdrawn from the instrument and replaced by an equal amount of water. Under these circumstances the water showed a surface tension of only 58.5 dynes, (point B on the curve), not much different from that of the solution of glycerol which it replaced. Vigorous agitation increased the value,

but only to 63.4 dynes, (point C). The capillarimeter was then carefully cleaned and dried. After this, water in the capillarimeter gave its proper surface tension, 72.6 dynes, as shown by point D on the curve.

This behavior would lead one to believe that during the first part of the experiment glycerol was adsorbed on the glass walls of the capillary and was not all removed, either by agitation or by the removal of the solution.

Another experiment of the same type showed, in addition, the following interesting fact. After the solution had stood in the capillarimeter over night, during which the surface tension fell from 70.6 dynes to 56.9 dynes, the solution was removed and water was substituted. When the amount of water in the capillarimeter was such that the meniscus stood in a part of the tube below that point at which the solution of glycerol meniscus had stood, the surface tension observed was 56.8 dynes. When more water was added, so that the meniscus came to rest at a point above that at which the solution meniscus had stood, the value observed for the surface tension was 72.2 dynes, very nearly the value to be expected for pure water. Since the water was added through the wide arm of the capillarimeter the surface of the meniscus was not changed by the addition, the meniscus was simply raised to a higher level. This tends to confirm the idea that glycerol is adsorbed on the glass walls in that portion of the tube in contact with the solution and is only removed with difficulty by agitation or by washing with water.

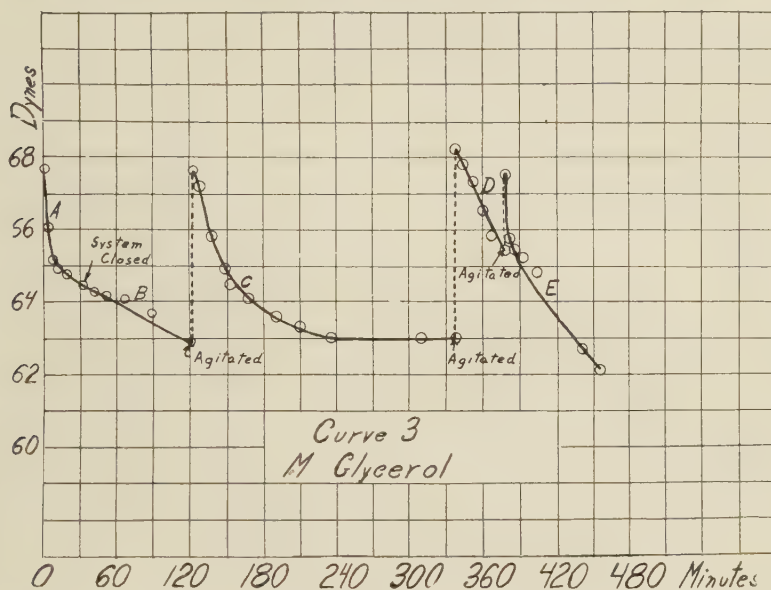
At least three later experiments confirmed these results as far as rate of fall is concerned. The time elapsing before the fall started and the effect of agitation, however, were not always the same. Several experiments with solutions of glycerol of the same concentration as that used above, have failed to show any change in more than an hour. In such cases, when the fall did start, the rate with which it progressed was often very much more rapid than that shown in Curve 2. Sometimes when the fall had failed to start for an unusually long time it was caused to start by a gentle agitation. These facts lead one to believe that the phenomenon which is responsible for the fall had been proceeding during the period of inactivity, but that the meniscus for some reason or other was prevented from responding. Something in the nature of a metastable state developed. In these experiments we had every reason to believe that the capillary was clean, but the fact that no change took place could be interpreted as indicating that the tube was not entirely free from foreign matter.

Evaporation of Water. It seemed that the decrease in surface tension might possibly be due to evaporation of water from the meniscus, leaving a more concentrated solution of glycerol, with a resulting lower surface tension. Vigorous agitation should correct this condition, giving a higher surface tension.

In order to determine whether or not this is a probable explanation of the phenomenon we carried out experiments in a type of capillarimeter which could be opened or closed at will, (Fig. 4). When the capillarimeter is closed the atmosphere within it should become saturated with water vapor, there should be no more evaporation and no fall, from this cause at least.

These experiments were carried out at 40° instead of 20° in order that the atmosphere should become saturated with water vapor in less time. The results of such an experiment are shown in Curve 3.*

These results are not in accord with what we should expect if our observed variation were due to the evaporation of water. Closing the system would stop the fall of the meniscus, if the vapor phase is saturated with water vapor,



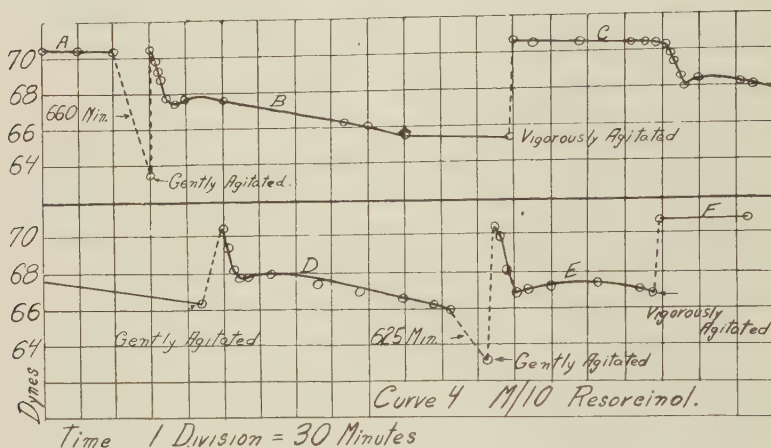
but it does not. After agitation of the solution in the closed capillarmeter by tilting it to and fro and the consequent restoration of the meniscus to its original condition, the small gaseous volume is surely saturated and there should be no fall at all. But falls occur repeatedly as shown. Not only this, but the fall denoted by part E of the curve is more rapid than that denoted by A, although during A the capillarmeter was open to the air, while, when E was started the instrument had been closed for five hours and forty-six minutes and the vapor phase was surely saturated.

On the other hand the results are in accord with what we would expect if the fall is due to an increased concentration of the glycerol at the interface between the solution and the glass walls, as well as at the solution-vapor interface.

Experiments such as resulted in Curve 2 indicate that if sufficient time be allowed some glycerol will become so firmly adsorbed on the glass walls that even vigorous agitation of the solution does not remove it. The agitation, by tilting, which we used in our closed system experiments, is of necessity comparatively gentle and quite inadequate to remove the adsorbed glycerol;

* We have drawn our curves to scale with care and believe we have included in them all information of interest to a reader. Therefore, we omit the extensive tabulations from which they were constructed.

even when pure water is substituted for the solution the low surface tension persists, presumably due to this adsorbed layer. However, if time has not been allowed for this firm adsorption of glycerol a gentle agitation will bring about uniformity in the concentration of the solution in the capillary. The original high surface tension, characteristic of the homogeneous solution against a clean glass surface, will then be observed. The time required for the glycerol to become thoroughly attached to the walls seems to vary, in the neighborhood of twelve hours being required when working at 20° , and a longer time when working at 40° .



Solutions of Resorcinol. The resorcinol which we used was Mallinckrodt's U.S.P. grade. Solutions of this material show a decreasing surface tension with time. In the results of the typical experiment which we give below we desire to call attention to the effect which the degree of violence of the agitation has upon the nature of the surface tension change which follows it.

The violence of the agitation which causes the surface tension to return to its maximum value after a fall has taken place, has a pronounced effect on the length of time which will elapse before the fall will start again. Part A of Curve 4 shows that the surface tension was constant for more than an hour after the solution was poured in the capillarimeter. A decided drop took place, however, during the next eleven hours. A gentle agitation then caused the surface tension to return to its maximum value. Part B shows that the drop started at once after this gentle agitation. After reaching a low value the solution was vigorously agitated, resulting again the maximum value. The two hour period which elapsed, after this more violent agitation, before the fall started is shown in part C. The effects of two more gentle agitations and a second violent agitation are shown in parts D, E, and F.

Periods of inactivity of this sort have been noticed by us in work with solutions of other organic substances. J. M. Johlin observed similar periods of inactivity with dilute solutions of sodium oleate and casein, but makes no

attempt to explain them. We recognize that our suggestion that a metastable state is established is inadequate as an explanation, but feel that it contains a hint worth following.

The suggestions we made in connection with our experiments with solutions of glycerol, are at least plausible here also. Let us assume that the lower surface tension values are due to the adsorption of the solute on the glass walls of the capillary and at the liquid-vapor interface of the meniscus. The gentle agitation serves to remix the solution in the meniscus but does not remove the adsorbed layer from the walls. The solution, now uniform, shows its appropriate surface tension, but adsorption in the meniscus starts at once and the surface tension soon falls. A vigorous agitation, on the other hand, not only remixes the solution in the meniscus but also removes the adsorbed layer from the walls. The fall is delayed by this treatment; perhaps a layer of the solute has to be adsorbed on the walls before the increase in concentration in the surface layer of the meniscus starts, or becomes effective in lowering the surface tension.

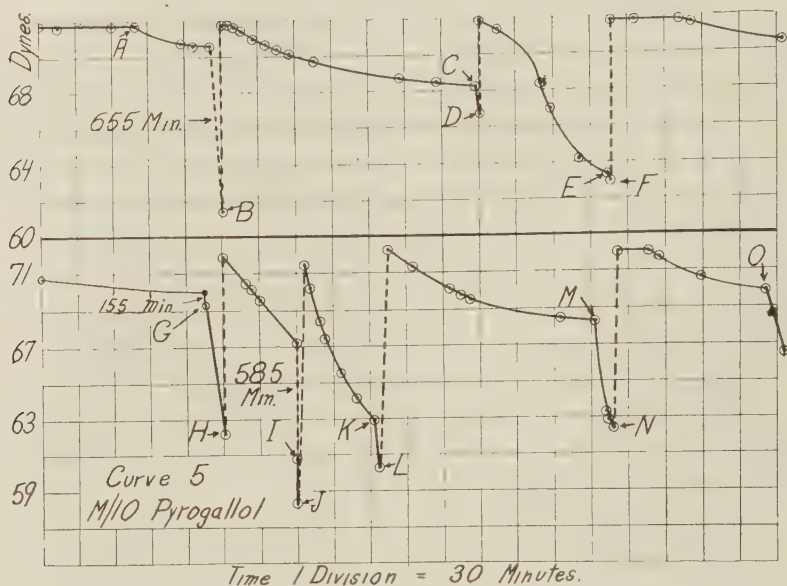
We observed a rather curious and interesting phenomenon with these solutions not shown in the curves. If, when the surface tension is at a minimum value, the meniscus is drawn down still farther in the capillary and then is allowed to ascend of its own accord, it rapidly comes back to the point at which it stood before it was lowered. No matter how far it is lowered, or how many times, the meniscus flies back to its original position as though drawn by a rubber band. If, however, the meniscus is gently forced a few millimeters above, not necessarily to its maximum point, and then lowered, it will fly up to the point to which it was forced. It does not hesitate as it passes its old minimum value. If the meniscus is forced above its maximum, or original value, it will fall to this point; if it is then drawn below it will rise to the same point.

A plausible explanation for this behavior is as follows. Water evaporating from the walls left wet by the descending column leaves a thin invisible layer of the solute. When the meniscus is drawn down and is allowed to fly back it will stop when it reaches the thin layer of the solute, because if it went further, it would dissolve the solute, become more concentrated and have a lower surface tension. When the meniscus is forced up a short distance it dissolves the solute from the walls and then will, if lowered, come back to the new and higher level where the walls are still coated with the comparatively dry solute.

Another of the puzzling phenomena which we noted in these experiments with resorcinol is the fact that a slight rise often takes place after a rather rapid fall. The rise, never amounting to more than a fraction of a dyne, is not always the same, nor does it always occur at the same point of the curve. After this rise has taken place the surface tension proceeds to fall slowly to some point below that at which it started to rise. Irregular results similar to these were noted by J. M. Johlin in work with solutions of gelatin. In the light of recent work of du Noüy, one may be justified in ascribing this slight rise, followed by a fall slower than the initial fall, to some sort of molecular orienta-

tion or rearrangement taking place in the surface layer. There is, however, no experimental proof that such an orientation would result in such a rise. We cannot ignore, on the other hand, a peculiar phenomenon which happens as consistently as this one has happened.

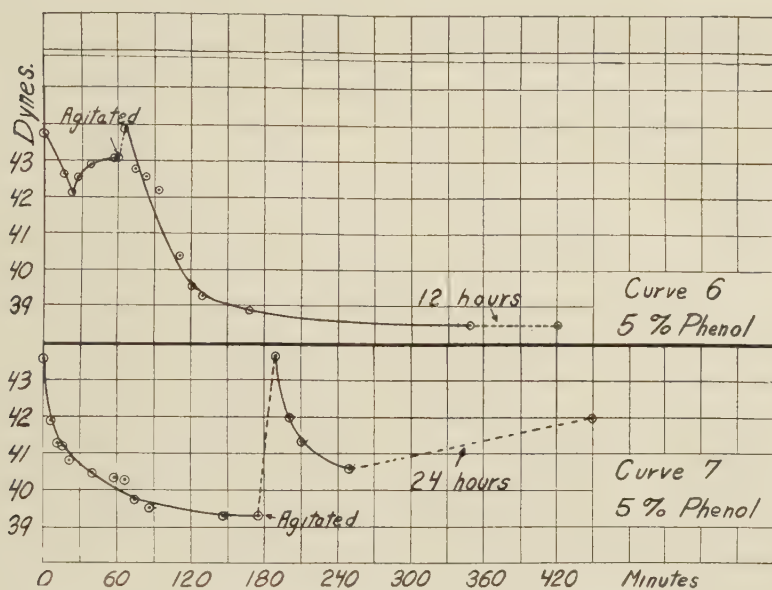
Solutions of Pyrogallol. The pyrogallol which we used was a standard C.P. grade.



At A and B vigorously agitated throughout the capillary. At C slightly agitated below the resting point. At D slightly agitated throughout the capillary. At E slightly agitated below the resting point. At F vigorously agitated throughout the capillary. At G vigorously agitated below the resting point. At H slightly agitated throughout the capillary. At I vigorously agitated below the resting point. At J slightly agitated throughout the capillary. At K vigorously agitated below the resting point. At L vigorously agitated throughout the capillary. At M vigorously agitated below the resting point. At N vigorously agitated throughout the capillary. At O slightly agitated below the resting point.

These results are of the same nature as those which we obtained with solutions of resorcinol and are readily explained by the same reasoning. A vigorous agitation throughout the tube is often followed by a period of inactivity before the fall starts. This is shown by the portions of the curve following the points B, F, and N. The duration of this period is not always the same, in fact, the fall sometimes starts almost at once but proceeds slowly as is shown by the curves following the points A and L. One reason for this difference undoubtedly lies in the fact that the agitation is not always of the same degree of violence; it is also probable that the adsorption on the walls has progressed to a greater extent in some cases than in others. According to our hypothesis

the vigorous agitation not only remixes the solution in the capillary but also removes the adsorbed layer from the walls. A gentle agitation, however, serves only to mix the liquid in the surface layer with the rest of the solution, and does not remove the layer from the walls. Such gentle agitation is invariably followed by a comparatively rapid fall as is shown by the steep portions of the curve following D, H, and J.

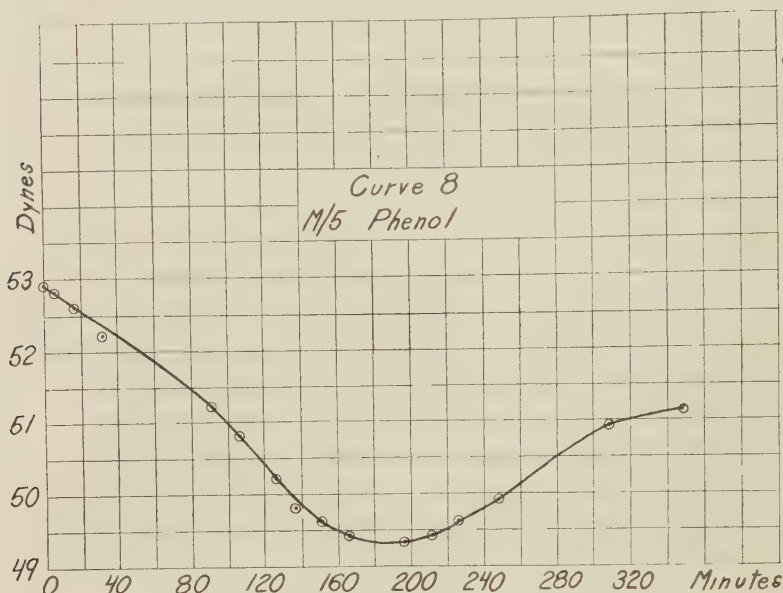


The fact that agitation, either gentle or vigorous, below the resting point of the meniscus in each case caused the liquid to come to rest at a point lower than that at which it had stood before is evident, (see points C, E, G, I, K, M, and O). This indicates that here has been lag in the fall, the decrease had not been quite keeping up with the adsorption of the solute. The agitation upset a metastable state and then the system moved to the proper point, as determined by the amount of adsorption which had taken place.

These experiments, showing the effect of agitation on the surface tension changes of solutions of glycerol, resorcinol, and pyrogallol, are, we feel, of significance. They are the most direct experimental evidence which has yet been offered in support of the theory that falling surface tensions can be caused by the adsorption of the organic solute at the liquid-glass interface as well as the liquid-vapor interface.

Solutions of Phenol. Variations in surface tension which are not readily accounted for on the basis of the theory which we have just outlined have been observed to take place with solutions of phenol. Many experiments were carried out with this substance in a vain attempt to reproduce conditions so that the same type of variation could be consistently obtained. The following curves illustrate the kind of irregularities which occur.

The fall in surface tension usually started at once, either with a new solution or with a freshly agitated one, although there was sometimes a short period of inactivity. The initial maximum values were reproducible without difficulty. In most of the experiments it was noted that, after a fall had taken place, the meniscus would slowly rise again to some point midway between the minimum and maximum values. This reversal would sometimes occur



within an hour after the start of an experiment, while in other cases several hours would pass without interruption of the steady downward trend. This rise is probably caused by the same phenomenon as that which was involved in experiments with resorcinol, and is perhaps of the same nature as that which caused the irregular results noted by J. M. Johlin with solutions of gelatin, and du Noüy with solutions of sodium oleate. At present we cannot account for this rise, and are unable to regulate the conditions which determine it.

Solutions of Other Substances. Surface tensions decreasing with time have also been noted and studied with solutions of oxalic, propionic, and succinic acids. As these studies discovered nothing beyond what we have described, details are omitted. Some other substances, which from analogy one would expect to form solutions showing decreasing surface tensions with time, as acetic acid, or sodium acetate, have very little effect on the surface tension of water.

Solutions showing an Increasing Surface Tension with Time

In preparing capillarmeters for experiments, after the cleaning and washing, they were dried by drawing dry air through them. In the preliminary stages of our work we employed an ordinary drying train, containing calcium chloride, soda lime, and cotton, and after passing through this, the air passed

through a rubber tube before entering the capillarmeter. We became suspicious of this tube and felt that it was at least possible that minute solid particles, or gaseous emanations from the rubber, might contaminate the walls of our instrument. In order to determine what effects such contaminations might have, we attached a rubber tube which had been in use for some time on a Bunsen burner. This was exceedingly effective and surface tension values obtained after this treatment were most erratic. We substituted glass tubes and ground-glass joints in such a manner that the air came in contact with no rubber before entering the instrument, thus effectually eliminating trouble from this source.

But evidently something from the rubber was one of the hitherto overlooked sources of error for which we were searching. We decided to investigate this. Accordingly we passed illuminating gas through a clean capillarmeter for two or three minutes, washed the capillarmeter twice with water, and then determined the surface tension of water. We were surprised to observe an increase with the passage of time. In one hundred and fifteen minutes the surface tension increased from 70.7 dynes to 72.2 dynes.

Illuminating gas is of indefinite composition, accordingly we turned to pure gases. We passed hydrogen, nitrogen, oxygen, carbon dioxide, sulfur dioxide, and methane through clean capillarmeters, determining the surface tension of water in them after each treatment. The values obtained differed but little from the surface tension of pure water. In no case could we detect an indication of an increase in surface tension with the passage of time.

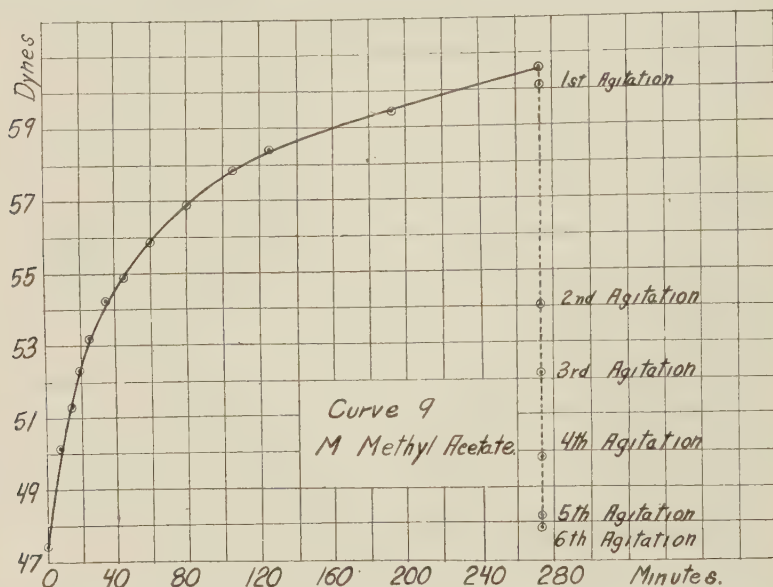
But these gases by no means exhaust the list of substances present in illuminating gas. Something from the gas must have clung to the walls. It might act in either of two ways. First, soiling the walls it would cause us to get too low a result, then, dissolving in the water the walls would become clean, and we should get the higher, correct value. Or, second, this foreign material might dissolve in the water at once and produce a lowering of its surface tension, and then it might evaporate from the meniscus until pure water was left, with its corresponding value.

Solutions of Amyl Acetate. Following this idea we turned to volatile substances which might be expected to evaporate from the surface of a water solution. Naturally we selected definite chemical compounds. Our first qualitative experiments were made with solutions of amyl acetate. We added one drop of amyl acetate to 100 cc. of water and put the solution in a capillarmeter, and were gratified to observe an increase in surface tension from 62.6 dynes to 69.6 dynes in half an hour. In observing the changing surface tension we were guided by our previous experience with falling surface tensions and so refrained from agitating the solution before each reading; we merely watched it climb.

This decided increase led us to study in a semi-quantitative manner the solutions of several different substances of the same type. The organic liquids used were purchased from Eastman Kodak Co., and unless so stated were

not purified further by us. Conductivity water was used in making up the solutions. These studies were only preliminary in nature, and the results should be considered as relative only.

Solutions of ethyl acetate, propyl butyrate, and butyl acetate show the phenomenon. A small increase in surface tension with time was noted with a dilute solution (about 2%) of ethyl alcohol. Aqueous solutions of amyl alco-



hol, propyl alcohol, and iso-propyl alcohol, displayed more pronounced increases with time. Ethylene dichloride and acetone when dissolved in water also gave definite increases in surface tension as time elapsed.

In general, the greater the initial lowering of surface tension caused by the solute the greater and more rapid is the increase following. With the substances we used, the higher the molecular weights the greater the effects on the surface tension of water. The solubility in water, however, decreases with increasing molecular weight and this fact limits the number of substances which we can use advantageously.

Solutions of Propyl Formate. A fifth molar solution of propyl formate showed an increase in surface tension from 47.8 dynes to 62.8 dynes in two hours. Agitation caused the surface tension to return to its minimum value from which a second increase took place.

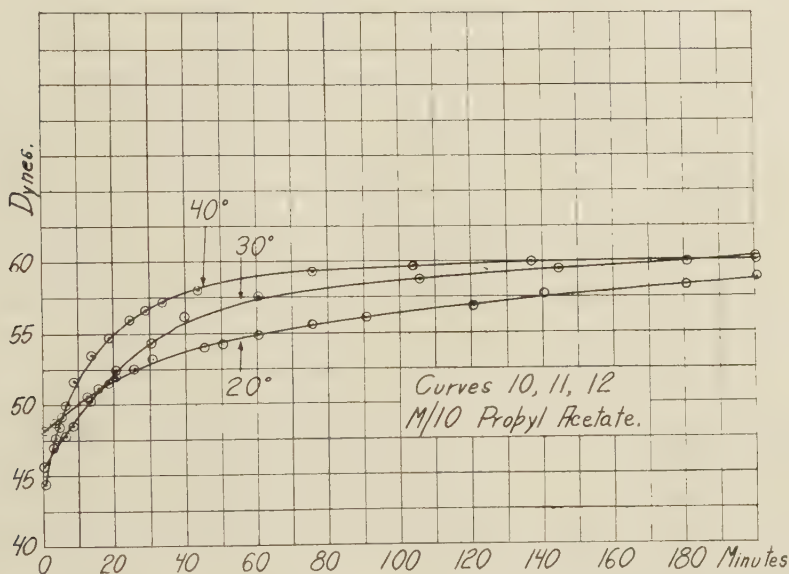
Solutions of Methyl Acetate. A molar solution of methyl acetate was used in several experiments intended as a more careful study of the rate of increase, and also of the effect of agitation in causing the drop from a maximum to a minimum surface tension. The results of a typical experiment with this solution are shown in Curve 9.

During the first two hundred and seventy-six minutes there was no agitation, and the surface tension increased from 47.5 dynes to 60.6 dynes. Then

the surface was agitated, by drawing it slowly up and down the tube once, after which a reading was taken. Then the liquid was again drawn up and down once, and a second reading was taken. This was repeated six times.

Manifestly the effect of agitation is cumulative and would finally result in a value practically the same as the initial reading.

Solutions of Propyl Acetate and Temperature Effects. Numerous experiments were carried out with solutions of this material in an attempt to find out the effect of different temperatures on the rate of the surface tension change.



The initial readings show, as was to be expected, the lowest surface tension at the highest temperature and the highest surface tension at the lowest temperature. Whatever the change which produces the increasing surface tension, it proceeds faster the higher the temperature. It looks as though we had reached the equilibrium condition at 40° after about 140 minutes. But the surface tensions at the lower temperatures are still ascending. The 30° curve crosses the 40° curve after 185 minutes and the 20° curve is gradually approaching that for 30°. We believe it will ultimately cross it. In short we feel justified by experiments in believing that the final equilibrium surface tension will be higher, the lower the temperature.

Quantitative Study. We felt that this phenomenon of rising surface tension was worth investigating quantitatively. It was necessary to choose one substance with which to work. It seemed desirable that the substance should show the phenomenon in as marked a degree as possible, that is, its solutions should have a surface tension much different from that of the solvent, water. It should be soluble enough to permit the study of a wide range of concentra-

tions; it should have a much higher vapor pressure than water, and not be readily hydrolyzed. Ethyl acetate was chosen as the solute best fulfilling these specifications.

Purification. Our stock ethyl acetate from the U. S. Industrial Chemical Co., was fractionated and that portion distilling over between 76.9° and 77.2° was reserved for further fractionation. After drying over phosphorous pentoxide for several hours this fraction was poured off and redistilled. A large amount which came over at nearly constant temperature was collected and preserved in a glass-stoppered bottle. The boiling point corrected to 760 mm. pressure varied from 77.11° to 77.20° . For this correction use was made of the dt/dp values obtained by J. Wade and R. W. Merriman.¹ The boiling point which they observed for pure ethyl acetate at 760 mm. was 77.15° . We found the density of our ester to be .9003 at 20° , which compares favorably with the density of .9005 recorded by Wade and Merriman for the same temperature.

A contraction in volume occurs when ethyl acetate dissolves in water and this contraction must be taken into account in making up solutions of definite concentration. We spent more time than we should have over this, actually determining experimentally this contraction. The details would not be of any general interest. We satisfied ourselves that making up solutions by diluting measured volumes of ester to calculated volumes of solution did not introduce a perceptible error in our results.

If the density of the vapor phase, air saturated with water and ethyl acetate, is much different from air saturated with water only, an error is introduced. (See formula ($\gamma = \frac{1}{2} \text{ hrg } (D-d)$)). The density of air at 20° saturated with water vapor is 0.0012. We made numerous determinations experimentally of the density of the vapor phase, air saturated with water and ethyl acetate over an M/2 ethyl acetate solution. The average of our results was, 0.001256. Error resulting from neglect of this correction was clearly negligible and so we used, $d = 0.0012$ throughout.

Ethyl Acetate. The following curves obtained with half molar ethyl acetate to show the type of rise we obtained and the limits within which one may expect to reproduce results.

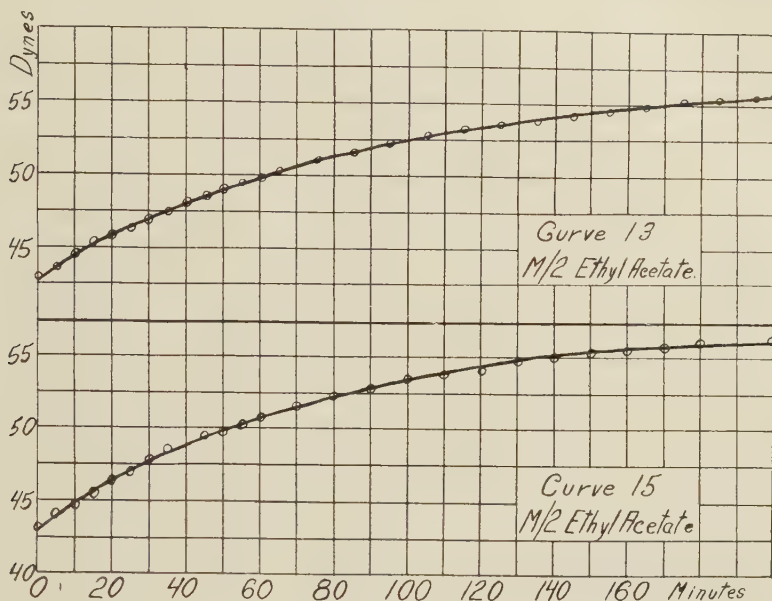
Agitation, by means of blowing and drawing, after each maximum value, caused the surface tension to return nearly to its original minimum value from which the usual rise again took place.

Curves 13 and 14 were obtained with both arms of the capillarimeter open to the air, while for curve 15 loose caps were hung over the open ends. The fact that these three curves are nearly identical is explained by the fact that the caps fitted loosely, allowing vapor to diffuse out as rapidly as it diffused up through the capillary.

We next joined the two arms of the capillarimeter with a piece of tightly-fitting, black gum, rubber tubing, and carried out the experiment resulting in curve 16. We thought that under these conditions the vapor phase would soon become saturated with the vapors of water and of ethyl acetate. An

¹ J. Chem. Soc., 101, 2438 (1912).

equilibrium would thus be reached at the meniscus, and there would be no further concentration change in this and consequently a constant surface tension would be obtained. The curves show that the presence of the rubber tubing made no noticeable difference. The rise proceeded at the same rate as before. The experiment was repeated many times but always with the same result. Even after being thus closed in the capillarmeter for several days the



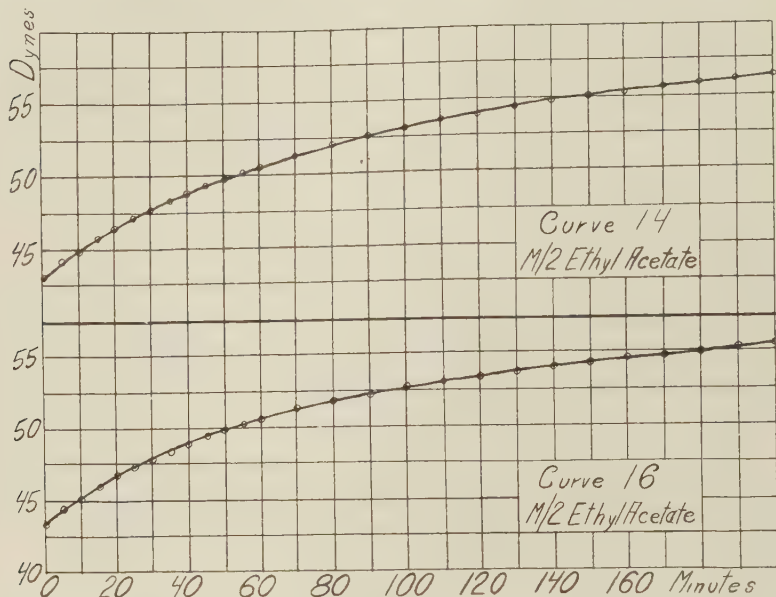
solution would show the usual rise from the minimum, obtained after an agitation, to a maximum value. This almost caused us to abandon the theory that the rise was due to evaporation of the ethyl acetate from the meniscus faster than it was replaced by diffusion from the interior.

Fortunately it occurred to us that perhaps the ethyl acetate was dissolving in the rubber, thus preventing the establishment of equilibrium at the meniscus.

Two pieces of black gum rubber tubing about three centimeters long, equipped with platinum hooks, were carefully dried and weighed. One of them was then suspended from a glass rod in a flask above distilled water, as shown in Fig. 5. The second piece was suspended above a half molar solution of ethyl acetate in a similar flask. After being in contact with the vapors in the flasks for some hours, the rubber tubes were again weighed. The original weight of the rubber tube which was suspended above water was 1.5420 gms. After eight hours and fifty-three minutes of contact with water vapor it weighed 1.5500 gms. The original weight of the rubber tube which was suspended above M/2 ethyl acetate was 1.5950 gms. After eight hours and fifty-three minutes of contact with the vapor above the solution it weighed 1.7500 gms., a gain of .1550 gms.

After twenty-three hours and thirty minutes the tube above the water showed a gain of .0165 gms., while the tube above the solution of ester for the same length of time, showed a gain of .1850 gms.

A similar experiment carried out with water and an aqueous solution of propyl acetate gave very similar results. Evidently rubber will take up large amounts of ester vapors. After being exposed to the air for several hours the



tubes again showed their original weights. This explains the fact that the closing of the capillarmeter with a rubber tube in experiment 16, caused no change in the rate of increase of surface tension. The tube did not close the system and prevent evaporation. It might as well not have been there.

Vapor lost by Diffusion. In order to find out whether or not the amount of vapor absorbed by the rubber tube was comparable with the amount which would ordinarily evaporate and diffuse out of the capillary tube of a capillarmeter, the following experiment was carried out. A capillary tube with a bulb at one end, as shown in Fig. 6, was filled with half molar ethyl acetate solution to within about 3.3 cm. of the top. Sixteen hours were allowed for the drainage and drying of the capillary walls above the meniscus. Owing to the short length of the tube above the meniscus, more ethyl acetate should evaporate and diffuse from this tube than from the capillary of any capillarmeter used. After the sixteen hour period the meniscus was 3.50 cm. from the top. The instrument was then weighed after different time intervals with the following results.

Loss after 10 hours	.0002 gms.
" " 15 "	.0005 "
" " 48 "	.0015 "
" " 72 "	.0027 "

After seventy-two hours the meniscus was 4.06 cm. from the top, a fall of about .56 cm.

This experiment proves that the amount of ethyl acetate and water which will evaporate and diffuse from a capillary, of the size used in our capillarmeters, is much less than the amount which the rubber tube is capable of absorbing in the same time.

Closed Capillarimeter. In order to close completely the capillarimeter and obtain saturation of the vapor and equilibrium at the meniscus, we made use of an instrument constructed as shown in Fig. 4. With the stopper out the system was open; with it in, it was truly closed.

The following curve is representative of the many which we obtained with solutions of different esters and alcohols in capillarmeters of this type.

In another experiment carried out in the same capillarimeter at 20° with half-molar ethyl acetate, the initial surface tension was 42.3 dynes. After one and a half hours with the system open the value increased to 54.0 dynes, the system was then closed and after another hour and a half the surface tension had decreased to 42.4 dynes. The system was again left open for one and a half hours, and the surface tension increased to 54.4 dynes. The glass stopper was then inserted, and twelve hours later the surface tension was 40.2 dynes.

The fact, that the surface tension stopped increasing and started to decrease as soon as the system was closed with a glass stopper, must be due to the gradually increasing concentration of the ester in the vapor phase. It was often observed that the value obtained for the surface tension of a solution, after the capillarimeter had been closed for some time, was lower than the value shown by the solution immediately after being poured into the capillarimeter. This is probably due to the difficulty of obtaining a reading of the position of the meniscus, before a slight rise has taken place.

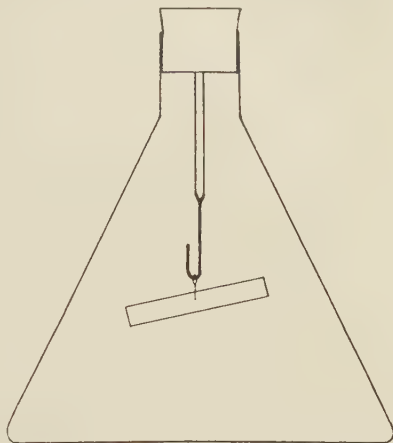
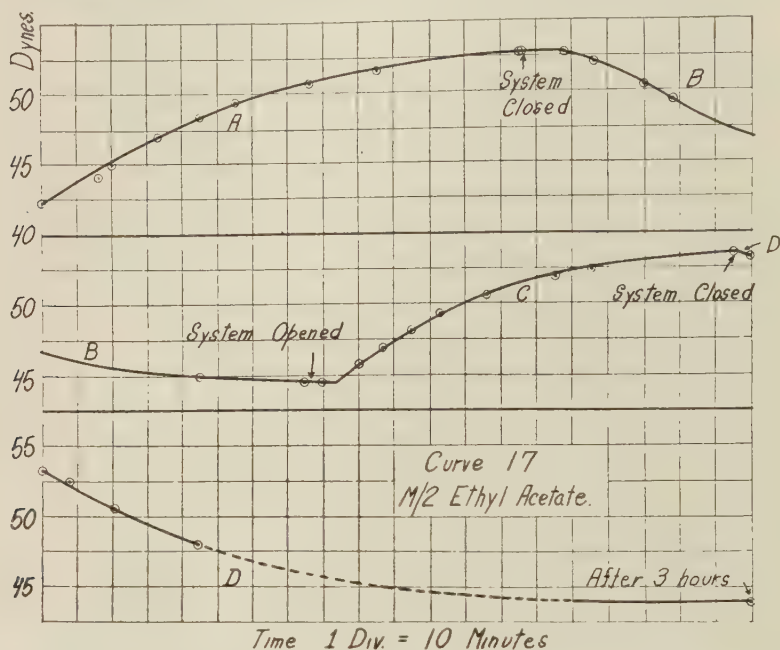


FIG. 5



FIG. 6

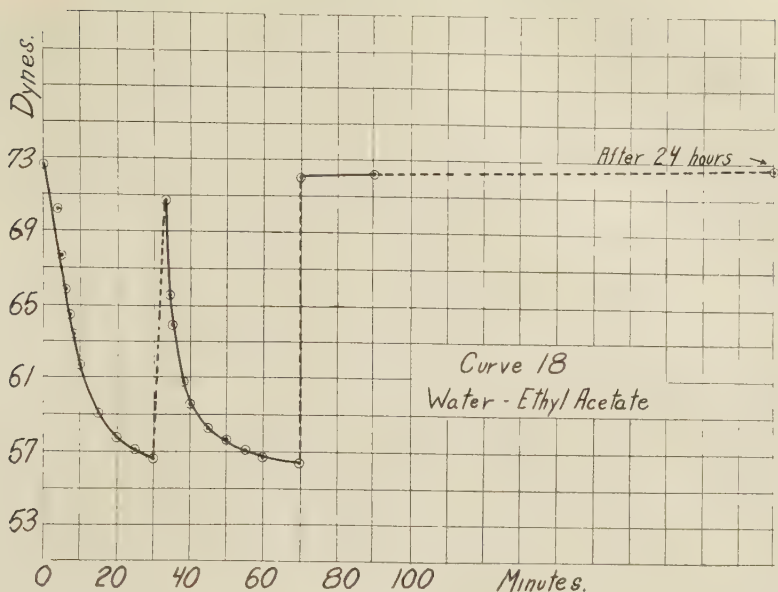
Experiments in Side Arm Capillarimeter. Convincing evidence that the extremely small amount of ethyl acetate which does evaporate and diffuse through the capillary in one of our instruments is sufficient to cause the observed change in surface tension is given by the following experiment. A capillarimeter was constructed with a side arm attached above the capillary tube, as shown in Fig. 3. Pure water was placed in the main part of the in-



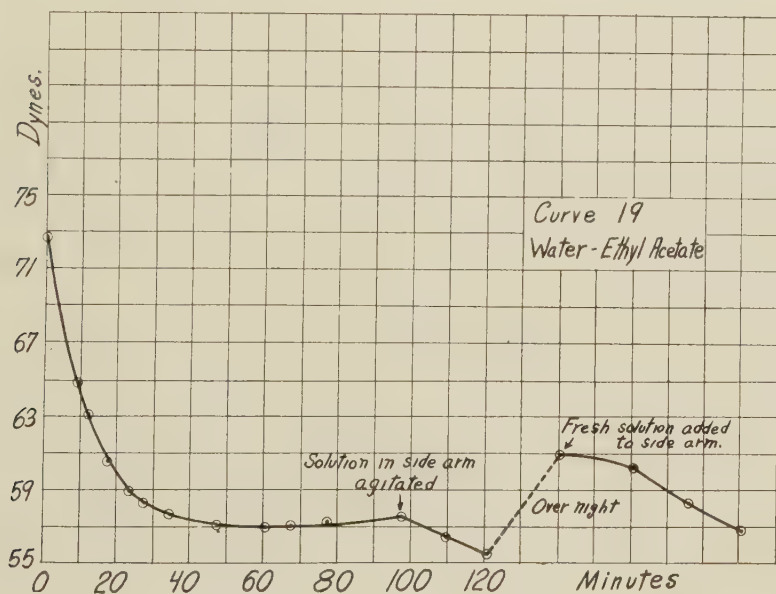
strument and its capillary rise noted. Half molar ethyl acetate was then placed in the side arm and the following curve was obtained.

The fall is obviously due to the evaporation of the ethyl acetate from the side arm, diffusion through the capillary and its solution in the surface. After 30 minutes, when the value 56.6 dynes had been reached, the solution in the capillary was violently agitated with the result that the surface tension rose to 70.8 dynes. This was evidently because the comparatively concentrated layer in the meniscus got stirred into the body of the liquid. At 70 minutes we removed the ethyl acetate solution from the side arm and agitated the solution as before, we immediately got a value of 72.1 dynes which rose to 72.6 in 24 hours.

We have shown that the actual amount of ethyl acetate which would evaporate and diffuse through our capillary tubes is very small, less than .0002 gms. in ten hours or about .00001 gm. in thirty minutes in a tube the length of this one. Yet this extremely small amount was sufficient to cause a drop in surface tension of sixteen dynes. This is a convenient and striking way to demonstrate the known fact that minute traces of some substances produce marked effects on surface tension.



Rise after Minimum Value. In many of the experiments carried out as described for Curve 18, it was observed that after the minimum value was reached a slight increase would take place. More careful investigation showed that this increase always took place if the experiment was continued long enough, providing that the liquid in the side arm was a solution of the ester and not the pure ester. The magnitude of the changes involved is shown in the following characteristic curve.



This behavior is readily explained. The meniscus is gaining ethyl acetate due to evaporation from the side arm and is losing it as it diffuses downward into the liquid. Simultaneously the evaporation in the side arm is diminishing due to the the diminishing concentration in that surface. These effects all balance at the minimum apparent on the curve at 60 minutes. After this the meniscus loses by diffusion faster than it gains from the side arm. But when we renewed the surface in the side arm by agitation, the curve took a downward trend again.

Diffusion through Gases. Measurements such as these could readily be developed into a convenient method of studying the rates of diffusion through gases in capillary tubes. They could also be used to measure the rates of diffusion from the surface into the body of the liquid.

Diffusion through Liquid. In an ordinary open capillarimeter (Fig. 2) we placed some half-molar ethyl acetate. We then carefully inserted some pure water in the capillary tube, enough to cover the solution meniscus with a water layer about one centimeter thick. The only way in which the ester can affect the surface tension of such a system is by diffusion up through the water to the meniscus. Of course a little of the solution is likely to stick to the walls of the tube and thus contaminate the water as it is poured in. With careful manipulation, however, such effects are very small. Several experiments of this sort, at 20°, did not show any change in several hours. In order to hasten diffusion we then carried out experiments at 40°. The following results are typical.

Time elapsed.	Surface tension
0 minutes	68.8 dynes
47 "	68.4 "
215 "	68.5 "
1080 "	68.7 "
solution agitated	52.3 "

The surface tension remains nearly that for pure water, not enough ester molecules diffusing through the water in over eighteen hours to cause any lowering. After this interval the solution was agitated by drawing it down out of the capillary several times. Enough ester was thus mixed with the water to cause a large lowering in the surface tension. Evidently diffusion through the liquid phase must be very slow. This method is capable of development and may be of some practical value.

Incidental Observations

It was our original purpose to discover, investigate and report as many sources of error as possible connected with the measurement of surface tension by the capillary tube method. We shall, therefore, now present a few incidental observations which were made.

Drops. It often happens that a drop (ring of liquid) forms at some distance above the meniscus. Following is a description of one instance. It occurred when working with half molar propyl acetate. In the initial reading the top of the meniscus, A (Fig. 7) stood at 13.000, while the bottom of the

drop, B, stood at 13.200 on our cathetometer scale. Twelve minutes later the meniscus A had ascended to A', 13.180, while the drop had remained stationary. Immediately after taking this reading the drop B suddenly disappeared and at once the meniscus rose to A'', 13.260, slightly above the place where the top of the drop had been. The drop is formed by drainage of the solution left on the walls after wetting, and just as in the well-known phenomenon of "tears on strong wine," it rapidly becomes

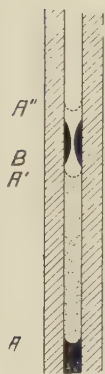


FIG. 7

more nearly pure water by the evaporation of the ester. Evaporation is going on at the surface of the meniscus also, and, as a result, the meniscus rises until it approaches near enough to the drop to draw it to itself, or to be drawn up by the drop, resulting in a sudden increase in surface tension due to the more nearly pure water of which the drop is composed.

The same phenomenon has often been noted in a slightly different form. The whole length of capillary having been wet by the solution, a drop was seen to form as at A in Fig. 8. The tube being a rather wide one the drop began to fall slowly. The fall was followed by the telescope and it was noted that when it was within a few millimeters of the meniscus it suddenly disappeared



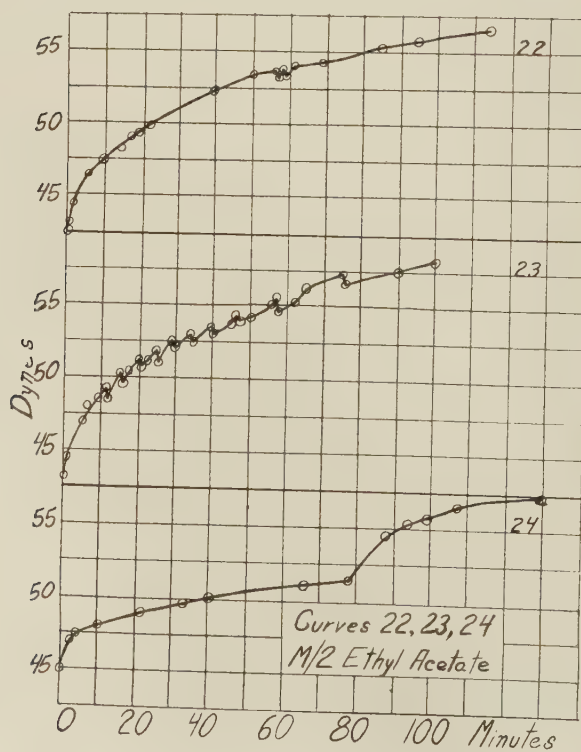
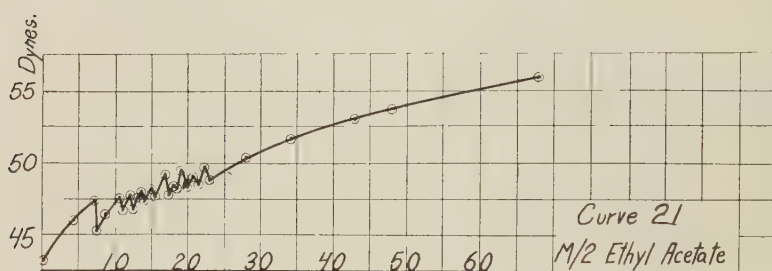
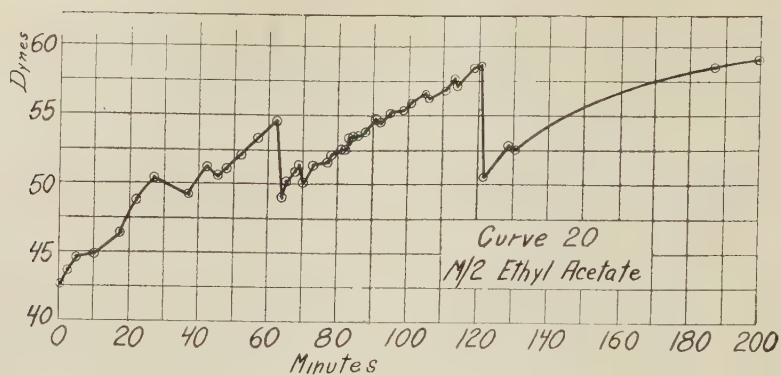
FIG. 8

downward into the meniscus, which in turn, ascended quickly to a new height. Not nearly enough liquid descended in the drop to account for the rise noted. During its gradual fall the drop had become more nearly pure water, due to the evaporation of the ester, and when near enough to the meniscus to be pulled into it, it simply exerted its proper surface tension.

It is probable that small drops are formed on the walls of the tube above the meniscus fairly often. They may be too small to be seen, but large enough to be the cause of the rapid increases sometimes noted, and unaccounted for in any other way.

Throbbing. Many of our experiments have failed to give us a smooth, uniform rise. During its ascent, the meniscus would often pause, fall rapidly and then rise slowly as before. When a point, slightly higher than the one from which the fall had taken place before, was attained, another drop followed by another rise, took place. This phenomenon was often repeated many times in the course of an experiment. The range of these pulsations varied, from a small fraction of a dyne in some instances to four or five dynes in other. We found it convenient to refer to this behavior as a "throbbing."

The frequency of this throbbing, as well as the range, varied a good deal. Sometimes several minutes would elapse between throbs, while at other times they would follow each other in rapid succession. Constant vigilance was the price of a numerical record of this phenomenon. Several experiments were carried out, during which, careful watch was kept on the meniscus, a reading being taken every time that it changed the direction of its motion. Several of these records will be given to show the extreme lack of regularity in these variations.



This throbbing was evident in probably thirty per cent of the experiments which involved an increasing surface tension. It seems much more apt to occur if the increase starts out rapidly than if it starts slowly. It very seldom occurs in an experiment involving a decreasing surface tension, although we have noted it in a few such experiments.

As a possible explanation we offer the following suggestion. We have learned by experience that it is exceedingly difficult to make the surface of a capillary tube (or any other surface) strictly clean, and yet more difficult to keep it so, even for a short time. It is perfectly possible that, in spite of all our precautions our tubes were not entirely clean. Then as the meniscus rises it will dissolve contamination until the surface acquires a lower surface tension, compelling a fall. Its subsequent ascension is not hindered in the interval through which it dropped for the walls were cleaned by the motion of the liquid. Therefore the meniscus rises rapidly and uniformly through the distance it fell, and rises higher until it gathers up more contamination; enough to produce the next fall.

Again the phenomenon may be due to molecular rearrangements in the surface film. This idea of definite molecular orientations is truly fascinating. If we give free rein to our imagination, as seems to be the fashion just now, we may conceive that the molecules of ethyl acetate in a dilute solution travel around in schools, or molecular swarms, and when such a swarm arrives at the meniscus there is a corresponding drop in the surface tension. This idea is not without support. For instance, J. M. Johlin¹ makes the statement: "Evidence of rearrangements at the surface is indicated by the frequent throbbing or pulsating of the meniscus, without necessarily resulting in any immediate change in surface tension—a fact invariably observed in all experiments with a wider capillary."

We are inclined to be conservative and, while admitting the possibility of such an explanation, prefer not to commit ourselves at present.

Effect of Size and Shape of Capillarimeters. It became evident to us that, although the initial, minimum values were easily reproducible, the rate of increase of surface tension varied with different capillarimeters. With instruments of nearly the same shape and dimensions the differences in rate were not great. But with capillarimeters of radically different type greater variation is evident. For example, the rise noted in capillary D when used in the form illustrated in Fig. 2 was more rapid and a higher maximum was reached than when the tube was used in the form illustrated by Fig. 4.

This variation is adequately explained on the basis of the evaporation theory. The air and vapor in the tube above the meniscus is stagnant, that is, it is not readily removed by external air currents. It is natural to suppose that it is more stagnant in an instrument of the type shown by Fig. 4 than in the kind illustrated by Fig. 2, for in the former case there is only one opening to the atmosphere while in the latter case there are two.

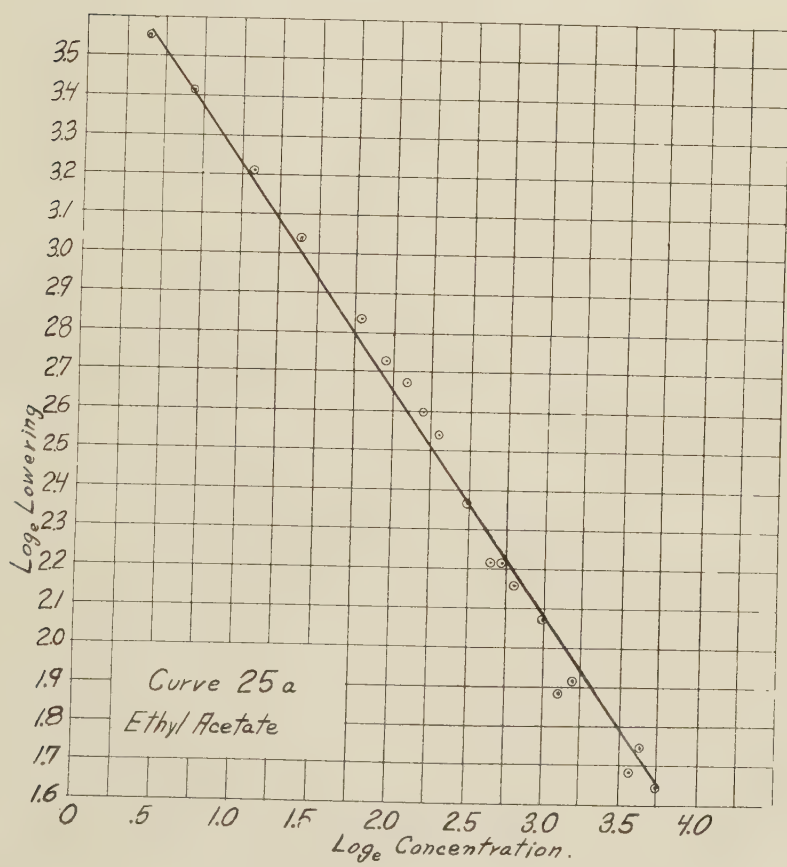
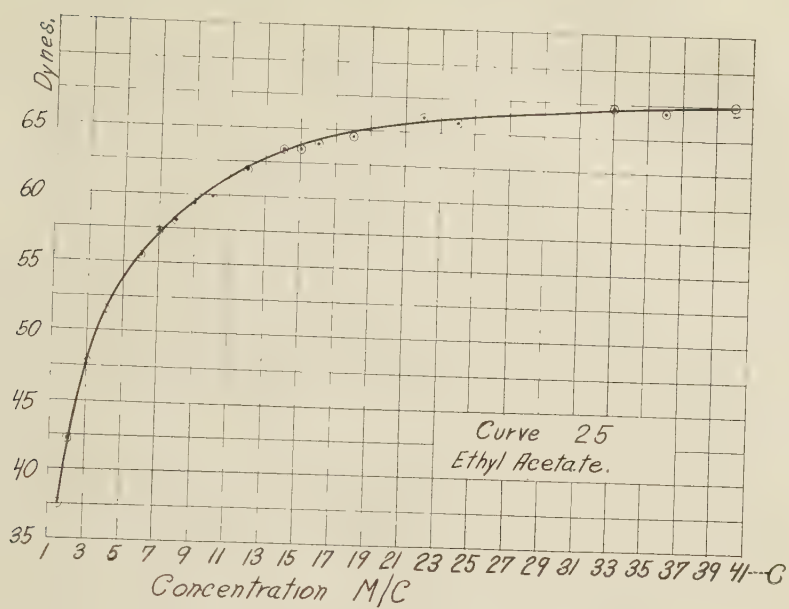
¹ J. Phys. Chem., 29, 282 (1925).

It is more difficult, however, to account for the fact that in capillarimeters which are alike except for the diameter of the capillary, the phenomenon proceeds more rapidly in the capillary of the smaller diameter. If simple diffusion of gases was the controlling factor in the velocity of the change we would expect it to be greater in the larger tube. At present we have no plausible explanation to offer.

Concentration in the Surface. We carried out experiments in which we determined the true surface tension of ethyl acetate solutions of different concentrations. In obtaining the true surface tensions of these solutions two methods are available. Experience has shown us that the best method is to use a closed capillarimeter and to allow sufficient time for the atmosphere to become saturated with the vapor of the solution. The second method is simply to note the initial minimum value before any change with time has taken place. This method usually gives values slightly higher than the first, due to the difficulty of determining the initial point of a slowly moving meniscus. With careful but rapid manipulation, however, it is possible to check, very closely, results by the two methods. In the following table the method or methods used, are stated in each case. Several different capillarimeters were used in these experiments, no difficulty being experienced in checking minimum values with the different instruments. Temperature $20.0^{\circ} \pm 0.1^{\circ}$.

Concentration Molar		Surface tension	Method	Lowering from water value
M/1.5	.6666	37.6 dynes	open tube	35.1
M/2	.5000	42.2 "	both methods	30.5
M/3	.3333	47.9 "	both methods	24.8
M/4	.2500	51.5 "	both methods	21.2
M/6	.1666	55.6 "	closed tube	17.1
M/7	.1428	57.4 "	open tube	15.3
M/8	.1250	58.1 "	both methods	14.6
M/9	.1111	59.3 "	closed tube	13.4
M/10	.1000	59.9 "	open tube	12.8
M/12	.0833	61.9 "	open tube	10.8
M/14	.0713	63.5 "	open tube	9.2
M/15	.0666	63.5 "	open tube	9.2
M/16	.0625	64.0 "	both methods	8.7
M/18	.0555	64.7 "	both methods	8.0
M/22	.0454	66.1 "	open tube	6.6
M/24	.0416	65.9 "	closed tube	6.8
M/33	.0333	67.3 "	open tube	5.4
M/36	.0277	66.9 "	closed tube	5.8
M/40	.0250	67.5 "	both methods	5.2

Plotting these results we obtain Curve 25. We can read off from this curve directly the concentration of the solution which must correspond to any particular surface tension. It would be going too far to make the simple assumption that the concentration at the meniscus is the same as in the interior of the



liquid under these conditions. But it may be. Whatever the conditions actually are we have here an interesting relationship which will be of help in elucidating them.

H. Freundlich¹ gives an equation connecting surface tension lowering with concentration.

$$\Delta = \frac{\gamma_m - \gamma_1}{\gamma_m} = Kc^{1/n}$$

Where Δ is the lowering of surface tension to be expected for any concentration c ; γ_m is the surface tension of the pure solvent; γ_1 the surface tension of the solution; K and $1/n$ are constants. That our experiments agree essentially with the formula is shown by the nearly straight line obtained when the logarithm of the concentration is plotted against the logarithm of the lowering. Curve 25a.

Rate of Increase. We have advanced the theory that increase of surface tension with time is due to evaporation of solute from the surface faster than it is replaced by diffusion from the body of the solution. Certain deductions from this theory are possible. When an apparent maximum surface tension is reached the rate at which the surface is losing solute by evaporation is equal to the rate at which it is gaining solute by diffusion. But this must be only an apparent maximum for, given time enough, practically all solute will reach the surface and will evaporate. The true maximum must always be the surface tension of pure water. Replenishment of the surface must be directly proportional to the concentration from which diffusion takes place. Consequently the increase in surface tension should be most rapid at the beginning and should fall off with time. This deduction has been abundantly verified.

It follows that when a solution of greater concentration, say $M/2$, has reached a point where it shows a surface tension corresponding to a lower concentration, say $M/5$, the adjacent layers have been impoverished and diffusion must proceed through a greater distance. Therefore the rate at which the surface tension of this solution increases should be less than the initial increase shown by an $M/5$ solution. We put this deduction to the test of experiment.

Our deduction is well justified. At the expiration of 60 minutes the $M/2$ curve showed the surface tension corresponding to an $M/5$ solution. Its slope at this time is obviously less than the initial slope of the $M/5$ curve. At the expiration of 60 minutes the $M/5$ curve showed a surface tension corresponding to an $M/10$ solution and its slope is less than the initial slope of the $M/10$ curve, and so on.

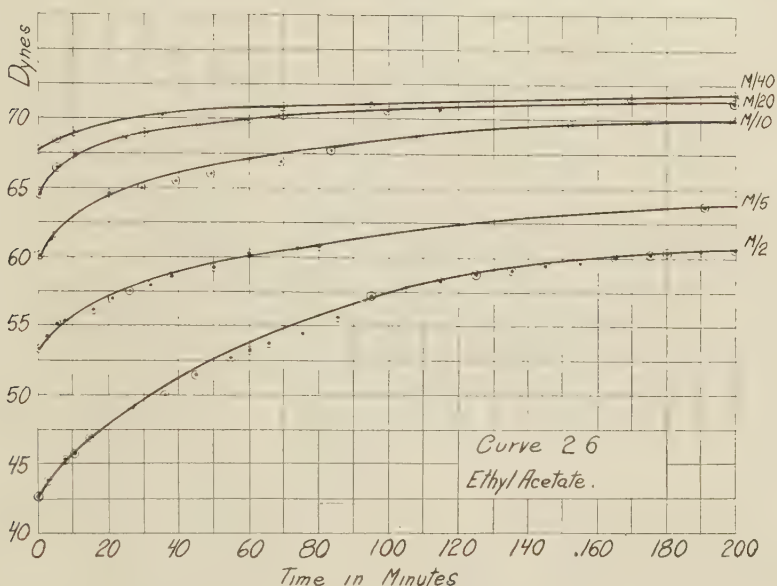
Hydrolysis. The substances with which we have worked hydrolyze, and if this occurs with sufficient rapidity our results give the surface tensions, not of solutions of our initial substances, but of the products of the hydrolysis.

We investigated this matter and found that the rates of hydrolysis varied greatly with different esters. In general, esters of lower molecular weight

¹ "Kapillarchemie," 90 (1922).

hydrolyze faster than those of higher. For example, a solution of methyl acetate hydrolyzes more rapidly than a solution of ethyl acetate of the same molecular concentration.

We proved by experiment that a solution of ethyl acetate in water hydrolyzes very slowly, too slowly to invalidate any of the results we have reported.



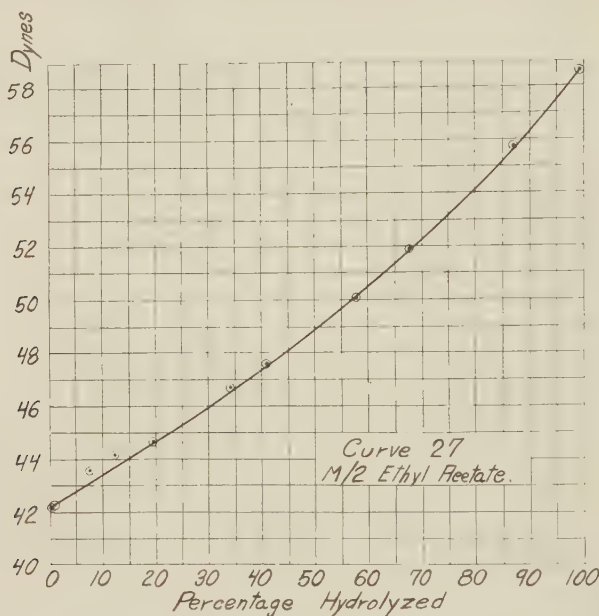
Two half molar solutions of ethyl acetate were made up and kept in glass stoppered flasks. These flasks were suspended in a constant temperature bath at $20.0^\circ \pm .5^\circ$. Samples were removed from time to time and titrated with standard barium hydroxide, using phenolphthalein as the indicator.

Solution 1			Solution 2		
Time elapsed		Per cent hydrolyzed	Time elapsed		Per cent hydrolyzed
0	Hours	.026	0	Hours	.026
12	"	.026	23.5	"	.033
48	"	.040	71	"	.13
136	"	.16	126	"	.16
181	"	.23	179.5	"	.26
252	"	.43	314	"	.83
496.5	"	1.36	483	"	1.85
665	"	2.43	657	"	3.33
827	"	4.00	4689	"	86.0

During the last five months solution 2 was kept at room temperature, several degrees above the temperature of the first part of the experiment.

We ran surface tension determinations on this 86% hydrolyzed solution and found an initial value of 55.5 dynes which increased to 58.2 dynes in 13 hours. Thus, when the solution is hydrolyzed, the minimum value is higher and the maximum value is lower than when it is fresh and not hydrolyzed.

This experiment, and several others, showed us that surface tension of solutions of esters increases as hydrolysis progresses. It is therefore possible to plot a curve, surface tension against degree of hydrolysis, from which it



will be possible to read directly the degree of hydrolysis corresponding to any particular surface tension. Of course it will be necessary in making or using such a curve to deal only with the minimum or true surface tension of any particular solution. As has been explained, this is best obtained by the use of a closed capillarimeter.

We obtained data for such a curve by making measurements upon an M/2 ethyl acetate solution which we caused to hydrolyze at a convenient rate by warming. Care was taken to allow no change in concentration due to evaporation. The degree of hydrolysis was determined by the usual barium hydroxide titration, carried out simultaneously with the measurement of surface tension. The value corresponding to a completely hydrolyzed solution was obtained by making up a solution of ethyl alcohol and acetic acid in the proper proportion to form a 100% hydrolyzed solution. Titration showed that this solution corresponded to 99.8% hydrolysis.

This is capable of being developed into a method for measuring the degree of hydrolysis of solutions of esters. Experiment has shown us that the surface tension of solutions of substances such as ethyl acetate may be readily determined to within 0.4%, with ordinary instruments and technique. We ob-

served that as a half molar solution of ethyl acetate changed in hydrolysis from 0% to 100% the surface tension underwent a total increase of 16.5 dynes. Our measure of the hydrolysis by the surface tension method was then accurate to within approximately $\pm 2.4\%$. ($.4/16.5 \times 100 = 2.4\%$)

The rate of any chemical reaction, resulting in a sufficiently large change in the surface tension, can be followed by this method.

Summary

(1) The decrease of surface tension with time, of solutions of sodium oleate, sodium glycocholate, and glycerol, as observed by earlier workers, has been confirmed. We have demonstrated that the same phenomenon occurs with solutions of other substances such as, phenol, resorcinol, pyrogallol, propionic acid, valeric acid and succinic acid.

(2) We have obtained experimental evidence in support of the theory that this phenomenon is caused by the adsorption of the organic solute at the glass-solution interface as well as at the vapor-solution interface.

(3) Contrary to the opinion of du Noüy we have shown that the phenomenon may be observed and adequately studied by the capillary rise method. Several of the facts which we have found could hardly be observed in any dynamic method of measuring surface tension.

(4) We have observed, perhaps for the first time, that solutions of certain esters and alcohols show an increase in surface tension with time. With these solutions, after a rise to a maximum, the fresh surface formed by agitation displays the original minimum value, from which another rise will start at once. A careful study of such changes as they occur with solutions of ethyl acetate has been made.

(5) We have offered a plausible explanation of the phenomenon, and have obtained much experimental evidence in its support.

(6) We have demonstrated the necessity of using a closed capillarimeter in measuring the surface tensions of numerous solutions and have shown that rubber connections cannot be used.

(7) We have measured the surprisingly small quantity of solute necessary to produce extensive lowering of the surface tension in a new way, one of which may have some applications.

(8) We have suggested a method for estimating the rates of diffusion to and from surfaces, and for estimating the concentration at the surface of a meniscus.

(9) We have devised a method for estimating the degree of hydrolysis of a solution of an ester.

(10) In conclusion; we believe we have contributed in some slight measure, at least, to our knowledge of the possibilities and limitations of the capillary rise method of measuring surface tension.

